



## ACID BLEND FOR REMOVING ETCH RESIDUE ON SEMICONDUCTOR SUBSTRATES

The present invention relates to the fabrication of semiconductor devices and more particularly to a method for cleaning a semiconductor substrate after the formation of dry etch residues thereon.

### BACKGROUND OF THE INVENTION

The importance of minimizing contamination during semiconductor fabrication processes has been recognized since the early days of the industry. As semiconductor devices have become smaller and more complex, cleanliness requirements have become increasingly stringent, especially for devices with submicron critical dimensions, because the ability to reliably create multi-level metallization structures is increasingly vital. The importance of cleaning and conditioning steps during the device fabrication process is also emphasized because small-scale residues that may not have seriously affected the performance of devices with large geometries may result in disabling defects in submicron devices.

Dry etch processes play a key role in developing multi-level metallization structures on semiconductor substrates. The step of transferring the desired pattern from the photoresist into the substrate is often accomplished via a dry etch process. While dry etch processes are effective for selectively etching the substrate in only the areas not masked by photoresist, these processes have a tendency to leave behind residues on the substrate. Although these residues may serve a beneficial role during a dry etch process, they are undesirable after the completion of the dry etch process. In back end of the line processes, where both dielectrics, such as  $\text{SiO}_2$ , and metals, such as Al or W, are

present, the residues left behind by dry etch processes may include both organometallic and organosilicate species. These undesirable post-etch residues are often difficult to remove without damaging the desired substrate features.

Current methods for removing dry etch residues have met with only limited success. Traditional cleans involving aqueous acid solutions can not provide a general solution for removing these residues, as these processes are not suitable for processing in the presence of metal lines. Current strategies often involve treating substrates with solutions containing hydroxylamine ( $\text{NH}_2\text{OH}$ ) and an organic chelating agent. These methods have shown some effectiveness but have significant drawbacks. These types of solutions can cause corrosion of exposed metal on the wafer and usually require long processing times at temperatures near 100 C. These hydroxylamine solutions are also expensive, as the chemicals are not only expensive to purchase but also typically require specialized disposal.

As the removal of dry etch residues grows increasingly troublesome in microelectronic device manufacture, there is a need for an effective method of removal of these residues which can be easily implemented in standard wafer processing equipment and has reduced costs for chemical purchase and disposal.

## SUMMARY OF THE INVENTION

The present invention provides an adaptable method for removing organometallic, organosilicate, and other residues from a semiconductor substrate following a dry etch process. A substrate previously subjected to a dry etch process is exposed to a conditioning solution to remove residues remaining after the dry etch. The composition of the conditioning solution can be varied to match specific applications. The conditioning solution generally contains a

source of fluorine, a complementary acid, a non-aqueous solvent, and preferably a surface passivation agent. One group of preferred conditioning solutions are solutions composed of HF,  $H_3PO_4$ , a polyhydric alcohol such as propylene glycol, and a surface passivation agent such as citric acid. In an alternate group of preferred embodiments the conditioning solutions are composed of HF, HCl, a polyhydric alcohol, and a surface passivation agent. The substrate is exposed to the conditioning solution for a sufficient amount of time to remove the undesired residues. After exposing the substrate to the conditioning solution, the substrate is rinsed, preferably by exposing the substrate to a rinse bath of a mildly acidic aqueous solution. Preferably this rinse step also involves bubbling a gas through the rinse bath to agitate the rinse bath.

Additional advantages and features of the present invention will be apparent from the following detailed description and drawings which illustrate preferred embodiments of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic cross-sectional view of a substrate with dry etch residues near a sample device feature.

Figure 2 is a schematic cross-sectional view of a substrate undergoing the process of a preferred embodiment of the invention.

Figure 3 shows the substrate of Fig. 2 at a processing step subsequent to that shown in Fig. 2.

Figure 4 shows the substrate of Fig. 2 at a processing step subsequent to that shown in Fig. 3.

Figure 5 shows the substrate of Fig. 2 at a processing step subsequent to that shown in Fig. 4.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In the following detailed description, reference is made to the accompanying drawings which form a part hereof, and in which is shown by way of illustration specific embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that structural and chemical changes may be made without departing from the spirit and scope of the present invention.

The terms "wafer" and "substrate" are to be understood as including any semiconductor-based structure having an exposed layer which may be effectively cleaned by the process of the present invention. Typically this will include semiconductor-based structures which have been dry-etched and have resultant organometallic and/or organosilicate residues on an exposed layer, but other structures may also be beneficially treated by the present inventive method. "Wafer" or "substrate" may include silicon-on-insulator (SOI) or silicon-on-sapphire (SOS) technology, doped and undoped semiconductors, epitaxial layers of silicon supported by a base semiconductor foundation, and other semiconductor structures. Furthermore, when reference is made to a "wafer" or "substrate" in the following description, previous process steps may have been utilized to form regions or junctions in the base semiconductor structure or foundation. In addition, the semiconductor need not be silicon-based, but could be based on silicon-germanium, germanium, or gallium arsenide.

The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is defined by the appended claims. When referring to solutions described herein, the term "percent" refers to the percent measured by weight, e.g., a 90% acetic acid solution is 90% by weight acetic acid.

Referring now to the drawings, where like elements are designated by like reference numerals, Fig. 1 depicts a semiconductor wafer 20 in an intermediate processing stage of a fabrication process. The wafer 20 comprises a substrate 22 with devices 24 located thereon. The devices 24 are covered by a dielectric layer 26 of SiO<sub>2</sub>, BPSG, or other suitable material which has a top surface 28. A device feature that has been formed by a dry etch process is formed on the substrate 22, either on or in the dielectric layer 26. For exemplary purposes, the device feature will be illustrated and described as a trench 30, which may be a via, but it should be understood that the invention is not limited thereto.

The trench 30 is formed in the dielectric material, and has sidewalls 32 and a bottom surface 34. If trench 30 represents an unfilled via allowing connection between metal levels, the bottom surface 34 may be composed of a metal such as aluminum or tungsten. The wafer 20 of Fig. 1 has been subjected to a dry etch process followed by a photoresist ashing or stripping process. Due to the dry etch process, residues 40, which may be, for example, organosilicate or organometallic residues, are present on the top surface 28 of the dielectric layer 26 and on the sidewalls 32 of the trench 30. If not removed, the residues 40 could prevent proper deposition of subsequent layers in the trench 30 or on the dielectric layer 26.

An embodiment of the present invention for removing residues is illustrated by Figs. 2 through 5. This embodiment uses a conditioning solution to cleanse the substrate surface after performance of a dry etch. The substrate 22 is exposed to the conditioning solution for a period of time sufficient to remove residues 40 from the substrate surface while minimizing the amount of material removed from exposed surfaces, such as metal lines, vias, or dielectric layers. The composition of the conditioning solution can be varied to match specific applications. The conditioning solution generally contains a fluorine source, a complementary acid, and a non-aqueous solvent. The complementary acid may be  $\text{H}_3\text{PO}_4$ ,  $\text{HCl}$ , or another acid or combination of acids which can serve as a pH suppressant. The non-aqueous solvent may be a polyhydric alcohol, such as propylene glycol or ethylene glycol. Alternatively, the non-aqueous solvent may be one of many other suitable organic solvents, including tetrahydrofuran, dimethylsulfoxide, propylene carbonate, or isopropyl alcohol. The conditioning solution preferably also contains a surface passivation agent. The surface passivation agent may be a carboxylic acid, such as citric acid, acetic acid, or EDTA. Other organic acids which are not carboxylic acids may also be suitable, such as ascorbic acid. Preferred conditioning solutions are solutions of  $\text{HF}$ ,  $\text{H}_3\text{PO}_4$ , and a polyhydric alcohol such as propylene glycol; solutions of  $\text{HF}$ ,  $\text{H}_3\text{PO}_4$ , a polyhydric alcohol, and a surface passivation agent; solutions of  $\text{HF}$ ,  $\text{HCl}$ , and a polyhydric alcohol; and solutions of  $\text{HF}$ ,  $\text{HCl}$ , a polyhydric alcohol, and a surface passivation agent such as citric acid.

Although  $\text{HF}$  is the preferred fluorine source, other fluorine sources may be effectively employed within the scope of this invention. For example,  $\text{NH}_4\text{F}$  might be employed as the fluorine source as long as the  $\text{NH}_4\text{F}$  was compatible with the other components selected for the conditioning solution. Similarly,  $\text{H}_3\text{PO}_4$  is not the only source of phosphate contemplated within the

inventive method. For example, phosphate salts which could dissociate to yield  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , or  $\text{PO}_4^{3-}$  might be appropriate depending on the other components in the conditioning solution. HF and  $\text{H}_3\text{PO}_4$ , however, are particularly preferred and convenient choices for the fluorine source and the complementary acid.

Referring to Fig. 2, the process of the present invention begins subsequent to the formation of devices 24, which may be transistors, capacitors, word lines, bit lines, or the like, on a substrate 22 of a wafer 20 and the formation of a dielectric layer 26 on the substrate 22. The dielectric layer 26 may be a silicon dioxide, borophosphosilicate glass (BPSG), phosphosilicate glass (PSG), borosilicate glass (BSG) or other dielectric layer, and may be deposited by chemical vapor deposition or other suitable means.

Fig. 3 depicts the next step of the process, in which a photoresist 42 is formed on the top surface 28 of the dielectric layer 26 by suitable means such as a spin-on technique. The photoresist 42 is patterned and developed, and a dry etch process is performed on the substrate using the patterned photoresist as an etch mask. At the end of the dry etch process, residues 40 are left behind on the substrate. Figure 4 depicts two possible locations where the residues might reside on the substrate once the remaining photoresist is removed by a suitable process such as ashing or stripping. Residues 40 might remain on the top surface 28 of the dielectric layer 26, or inside the trench 30, as shown in Fig. 4, or potentially at other locations on the wafer.

The wafer 20 is then subjected to the cleansing process of the present invention. The wafer 20 is exposed to a conditioning solution by any suitable method, which is typically a wet processing method. Suitable methods may involve immersion of the wafer 20, either singly or in combination with other



wafers, into a bath containing the conditioning solution, or by dispensing of the conditioning solution onto one or more wafers 20 as a stream or spray, so long as such dispensing of the conditioning solution results in exposure of the surface of the substrate to the conditioning solution for the desired length of time.

5 Other methods of treating substrates with the conditioning solution will be apparent to those skilled in the art. The wafer 20 is exposed to the conditioning solution for a time sufficient to remove residues 40 from the top surface 28 of the dielectric layer 26 and from the sidewalls 32 and bottom surface 34 of the trench 30. Residues 40 may be organometallic residues, organosilicate residues,  
10 other post-etch residues, or a combination of these residues. The cleansing method of this invention is effective for removal of these residues when present individually or in combination.

The wafer 20 may then be rinsed to prepare the substrate for a subsequent process step. In one embodiment, the substrate is rinsed with  
15 deionized water. In a preferred embodiment, the substrate may be exposed to an acidic rinse composed of an aqueous solution of a suitable acid. Carboxylic acids such as citric acid, acetic acid, or EDTA (ethylene diamine tetraacetic acid) are preferred for this embodiment. Other organic acids which are not carboxylic acids may also be used, such as ascorbic acid.

20 In another embodiment, the aqueous acid solution may be buffered to raise the pH of the solution to any desired pH level up to approximately pH 8. In yet another embodiment, anti-etch agents may be added to the rinse bath, such as ammonium lactate or boric acid. In another embodiment, the substrate may be rinsed by exposing the wafer to an organic solvent, such as an alcohol, a  
25 polyhydric alcohol (such as propylene glycol), a ketone, or a fluorocarbon. In another embodiment, the rinse may be carried out in a bath and the rinse bath

may be agitated by introduction of a gas. The agitating gas may be CO<sub>2</sub>, N<sub>2</sub>, or other gases which can be conveniently introduced into the rinse bath for agitation. In yet another embodiment, the solution may be agitated using megasonic energy. In still another embodiment, the solution may be agitated by manual or robot-controlled shaking of the vessel containing the rinse bath.

Use of the acidified rinse or buffered rinse greatly reduces the potential for unwanted consumption of the desired substrate materials after exposing the wafer to the conditioning solution. In embodiments where rinsing is accomplished with a rinse bath, a gas may be bubbled through the rinse bath. When the gas is CO<sub>2</sub>, introduction of the gas provides another means for acidifying the rinse water as well due to the formation of carbonic acid. When the rinse is already acidified, however, inert gases such as N<sub>2</sub> exhibit similar effectiveness to CO<sub>2</sub>. In some applications of this method, either the wafer may not be susceptible to the unwanted consumption of the substrate or additional loss of substrate material may not be critical. In these cases the wafer may be rinsed with deionized water.

In still another embodiment, the wafer may be pre-rinsed with a non-aqueous solvent prior to the rinse step. In one embodiment, the non-aqueous solvent is a polyhydric alcohol, such as propylene glycol. In another embodiment, the wafer is pre-rinsed with the same non-aqueous solvent used in the conditioning solution. After pre-rinsing the wafer with a non-aqueous solvent, the wafer may be rinsed with any of the rinses described above.

The exact nature and length of the rinse step may vary depending on the next process step the substrate will undergo. The wafer may be spin-dried after rinsing, if appropriate. The final structure of the wafer with the residue

removed is shown in Fig. 5. Further steps to create a functional circuit from the wafer 20 may now be carried out.

Typically the conditioning solution is composed of a fluorine source, a complementary acid, a non-aqueous solvent, and a surface passivation agent.

5 The fluorine source may be HF,  $\text{NH}_4\text{F}$ , or other suitable chemicals which can act as fluorine sources in the conditioning solution. The non-aqueous solvent is typically a polyhydric alcohol, such as propylene glycol or ethylene glycol. Other organic solvents may also be used, such as tetrahydrofuran, dimethylsulfoxide, propylene carbonate, or isopropyl alcohol. In many embodiments, propylene  
10 glycol is preferred due to considerations of low health exposure risk and ease of disposal. Blends of more than one alcohol may also be used. The complementary acid may be  $\text{H}_3\text{PO}_4$ , HCl, or another acid or combination of acids which may act as a pH suppressant. Preferably, the acid or combination of acids selected as the pH suppressant should be able to reduce the pH of the  
15 solution to below pH 2. The surface passivation agent is typically a carboxylic acid. Preferred carboxylic acids include citric acid, acetic acid, or EDTA. Other organic acids which are not carboxylic acids may also be used, such as ascorbic acid. Other surface passivation agents will be apparent to those skilled in the art. Other surface passivation agents could generally include chelants or reducing  
20 agents.

In one series of embodiments, the conditioning solution is composed of HF as the fluorine source, propylene glycol as the non-aqueous solvent,  $\text{H}_3\text{PO}_4$  as the complementary acid, and citric acid as the surface passivation agent. In one embodiment, the conditioning solution is composed of  
25 approximately 0.01 percent to approximately 5.0 percent HF, approximately 80 percent to approximately 95 percent propylene glycol, approximately 1 percent

to approximately 15 percent  $\text{H}_3\text{PO}_4$ , and approximately 0.001 percent to approximately 1.0 percent citric acid. In a preferred embodiment, the conditioning solution is composed of approximately 0.25 percent to approximately 0.3 percent HF, approximately 89 percent to approximately 94 percent propylene glycol, approximately 6 percent to approximately 7 percent  $\text{H}_3\text{PO}_4$ , and approximately 0.09 percent to approximately 0.50 percent citric acid. In a particularly preferred embodiment, the conditioning solution is composed of approximately 0.27 percent HF, approximately 91.5 percent propylene glycol, approximately 6.5 percent  $\text{H}_3\text{PO}_4$ , and approximately 0.25 percent citric acid.

In the above conditioning solutions the balance of the solution weight is made up by water. In many embodiments the conditioning solution is prepared by combining stock acid solutions which contain water, so a small amount of water may be present in the conditioning solution. It is preferred, however, that the water content of the conditioning solution be as low as possible.

In another series of embodiments, the conditioning solution is prepared by choosing HF as the fluorine source, HCl as the complementary acid, propylene glycol as the non-aqueous solvent, and citric acid as the surface passivation agent. In an embodiment, the conditioning solution is composed of approximately 0.01 percent to approximately 5.0 percent HF, approximately 80 percent to approximately 99 percent propylene glycol, approximately 0.003 percent to approximately 1.0 percent HCl, and approximately 0.001 percent to approximately 1.0 percent citric acid. In a preferred embodiment, the conditioning solution is composed of approximately 0.25 percent to approximately 0.3 percent HF, approximately 90 percent to approximately 98

percent propylene glycol, approximately 0.005 percent to approximately 0.009 percent HCl, and approximately 0.09 percent to approximately 0.5 percent citric acid. In a particularly preferred embodiment, the conditioning solution is composed of approximately 0.27 percent HF, approximately 97.5 percent propylene glycol, approximately 0.006 percent HCl, and approximately 0.25 percent citric acid.

Once again, the balance of the solution weight in the above conditioning solutions is made up by water. In many embodiments, the conditioning solution is prepared by combining stock acid solutions which contain water, so a small amount of water may be present in the conditioning solution. It is preferred, however, that the water content of the conditioning solution be as low as possible.

In another series of embodiments, the surface passivation agent may be omitted from the conditioning solution. The conditioning solution will still effectively remove any organometallic, organosilicate, and other post-etch residues if the surface passivation agent is omitted. In these embodiments, however, the risk of damage to features on the surface of the substrate is substantially increased. While these embodiments may be effectively employed, greater care must be taken with other reaction parameters such as processing time and temperature in order to avoid potential damage to desired surface features or the substrate.

Residue removal with the conditioning solution may be performed at temperatures of approximately 5 to approximately 60 degrees Celsius. Temperatures below 5 degrees Celsius may be used, but are not as favorable due to decreased residue removal speeds. As a result, at lower temperatures the conditioning solution may need to be applied to the substrate for longer periods

of time, leading to lower throughput in a production setting. Temperatures above 60 degrees Celsius may also be used. Preferably, the substrate is exposed to the conditioning solution at a temperature of approximately 35 to approximately 40 degrees Celsius. Exposing the substrate to the conditioning solution at a temperature of approximately 38 degrees Celsius is a particularly preferred embodiment of this invention.

Preferably, the substrate is exposed to the conditioning solution for a period of time sufficient to remove any undesirable dry etch residues from the surface of the substrate. This may involve an exposure of the substrate to the conditioning solution for periods of time ranging from about 10 seconds to about 60 seconds or longer depending on the exact nature of the substrate and the process temperature. Longer exposure times, such as about 180 seconds or longer, allow for greater removal efficiency of the dry etch residues but will also lead to lower throughput in a production setting. Also, depending on the exact nature of the substrate, longer exposures to the conditioning solution may eventually lead to removal of material from exposed features on the surface of the substrate, such as metal lines, vias, or dielectric surfaces. As a result, the optimal amount of time for exposure of a substrate to the conditioning solution will be substrate dependent. The preferred exposure time could be near 10 seconds, near 60 seconds, near 180 seconds, or a longer or shorter period of time depending on the exact nature of the target substrate as well as the residues targeted for removal.

The substrate may be treated with the conditioning solution by immersing the substrate in a bath of the conditioning solution. Alternatively, the substrate may be treated with the conditioning solution by dispensing the solution on to the substrate, such as by a spray technique. Other methods for

exposing the substrate to the conditioning solution will be apparent to those skilled in the art.

Without being bound by any particular theory, it is currently believed that several factors contribute to the effectiveness of this method for removing dry etch residues. It is believed that the carboxylic acid or other organic acid plays a role by passivating the surface of exposed metal lines, especially aluminum lines, which are on the surface of the substrate. In embodiments where the conditioning solution includes phosphoric acid, it is believed that the  $\text{H}_3\text{PO}_4$  and HF play complementary roles of aiding in the removal of organometallic and organosilicate residues, respectively. In embodiments where a pH suppressant is present, it is believed that the low pH of the conditioning solution tends to allow hydrofluoric acid present in the solution to exist as molecular HF and  $\text{H}_2\text{F}_2$ , as opposed to undergoing dissociation into  $\text{H}^+$ ,  $\text{F}^-$ ,  $\text{HF}^{2-}$ , or any of the other likely species produced when HF dissociates in solution. By preventing dissociation of the HF present in the conditioning solution, the HF is forced to remain in its molecular form which generally reacts much more slowly with substrate materials such as  $\text{SiO}_2$  or the aluminum lines likely to be exposed on a substrate surface.

An alternate theory which could explain the lack of reactivity with the aluminum lines is that the nature of the conditioning solution suppresses the solubility of aluminum fluoride. Aluminum fluoride is one of the likely products of any reaction involving aluminum lines on the surface of the substrate. Lowering the solubility of aluminum fluoride might cause this reaction product to build up at the surface of the aluminum lines and prevent further reaction.

As can be seen from the embodiments described herein, the present invention encompasses processes of removing dry etch residues from substrates having exposed areas of metal and/or dielectric. In one embodiment the

substrate is treated with/exposed to an conditioning solution composed of a  
fluorine source such as HF, a non-aqueous solvent, which is typically a  
polyhydric alcohol such as propylene glycol, a complementary acid, which could  
include  $H_3PO_4$ , HCl, or other pH suppressants, and a surface passivation agent,  
5 which is typically a carboxylic acid such as citric acid. The conditioning solution  
efficiently removes organometallic, organosilicate, and other dry etch residues  
with minimal impact on exposed features on the substrate surface.

The above description and drawings are only illustrative of preferred  
embodiments which achieve the objects, features and advantages of the present  
10 invention. It is not intended that the present invention be limited to the  
illustrated embodiments. Any modification of the present invention which  
comes within the spirit and scope of the following claims should be considered  
part of the present invention.

What is claimed is:



1. A method for removing dry etch residues from a semiconductor substrate comprising the steps of:

exposing a semiconductor substrate having dry etch residues thereon to a  
5 conditioning solution, wherein the conditioning solution comprises a fluorine source, a complementary acid, and a non-aqueous solvent.

2. The method of claim 1, wherein the fluorine source is HF.

3. The method of claim 1, wherein the fluorine source is  $\text{NH}_4\text{F}$ .

4. The method of claim 1, wherein the complementary acid is  $\text{H}_3\text{PO}_4$ .

10 5. The method of claim 1, wherein the complementary acid is a phosphate salt.

6. The method of claim 1, wherein the complementary acid is HCl.

7. The method of claim 1, wherein the complementary acid is a pH suppressant.

15 8. The method of claim 1, wherein the non-aqueous solvent is a polyhydric alcohol.

9. The method of claim 1, wherein the non-aqueous solvent is propylene glycol.

10. The method of claim 1, wherein the non-aqueous solvent is ethylene glycol.

5 11. The method of claim 1, wherein the non-aqueous solvent is tetrahydrofuran.

12. The method of claim 1, wherein the non-aqueous solvent is dimethylsulfoxide.

10 13. The method of claim 1, wherein the non-aqueous solvent is propylene carbonate.

14. The method of claim 1, wherein the non-aqueous solvent is isopropyl alcohol.

15. The method of claim 1, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, and the complementary acid is  $\text{H}_3\text{PO}_4$ .

15 16. The method of claim 15, wherein the HF, propylene glycol, and  $\text{H}_3\text{PO}_4$  are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 95 : 1 – 15.

17. The method of claim 15, wherein the HF, propylene glycol, and  $\text{H}_3\text{PO}_4$  are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 89 – 94 : 6 – 7.

18. The method of claim 15, wherein the HF, propylene glycol, and  $\text{H}_3\text{PO}_4$  are present in the conditioning solution in the approximate proportion of 0.27 : 91.5 : 6.5.

19. The method of claim 1, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, and the complementary acid is HCl.

20. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0.

21. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 93 – 98 : 0.005 – 0.009.

22. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.27 : 97.5 : 0.006.

23. The method of claim 1, wherein the conditioning solution further comprises a surface passivation agent.

24. The method of claim 23, wherein the surface passivation agent is a carboxylic acid.

5 25. The method of claim 23, wherein the surface passivation agent is citric acid.

26. The method of claim 23, wherein the surface passivation agent is acetic acid.

27. The method of claim 23, wherein the surface passivation agent is EDTA.

10 28. The method of claim 23, wherein the surface passivation agent is an organic acid.

29. The method of claim 23, wherein the surface passivation agent is ascorbic acid.

15 30. The method of claim 23, wherein the surface passivation agent is a chelant.

31. The method of claim 23, wherein the surface passivation agent is a reducing agent.

32. The method of claim 23, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is  $\text{H}_3\text{PO}_4$ , and the surface  
5 passivation agent is citric acid.

33. The method of claim 32, wherein the HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion of  
0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

34. The method of claim 32, wherein the HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and  
10 citric acid are present in the conditioning solution in the approximate proportion of  
0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.09 – 0.5.

35. The method of claim 32, wherein the HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion of  
0.27 : 91.5 : 6.5 : 0.25.

36. The method of claim 23, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface  
15 passivation agent is citric acid.

37. The method of claim 36, wherein the HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

38. The method of claim 36, wherein the HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 93 – 98 : 0.005 – 0.009 : 0.09 – 0.5.

39. The method of claim 36, wherein the HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion of 0.27 : 97.5 : 0.006 : 0.25.

40. The method of claim 1, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

41. The method of claim 1, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

42. The method of claim 1, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

43. The method of claim 1, wherein said exposure step further comprises immersing the substrate in the conditioning solution.

44. The method of claim 1, wherein said exposure step further comprises dispensing the conditioning solution onto the substrate.

45. The method of claim 1, wherein said exposure step is performed for a time sufficient to remove substantially all dry etch residues from the substrate.

5 46. The method of claim 1, wherein said exposure step is performed for approximately 10 seconds or longer.

47. The method of claim 1, wherein said exposure step is performed for approximately 60 seconds or longer.

10 48. The method of claim 1, further comprising rinsing the substrate after said exposure step.

49. The method of claim 48, wherein said rinsing step comprises exposing the substrate to deionized water.

50. The method of claim 48, wherein said rinsing step comprises exposing the substrate to an aqueous acid solution.

15 51. The method of claim 50, wherein the aqueous acid solution is a solution of a carboxylic acid.

52. The method of claim 50, wherein the aqueous acid solution is a solution of citric acid.

53. The method of claim 50, wherein the aqueous acid solution is a solution of EDTA.

5 54. The method of claim 50, wherein the aqueous acid solution is a solution of acetic acid.

55. The method of claim 50, wherein the aqueous acid solution is a solution of an organic acid.

10 56. The method of claim 50, wherein the aqueous acid solution is a solution of ascorbic acid.

57. The method of claim 50, wherein the aqueous acid solution is a solution of carbonic acid.

58. The method of claim 50, wherein the aqueous acid solution is buffered to a pH between approximately 4.0 and approximately 8.0.

15 59. The method of claim 48, wherein said rinsing step comprises exposing the substrate to an organic solvent.



60. The method of claim 59, wherein the organic solvent is propylene glycol.

61. The method of claim 48, wherein said rinsing step comprises exposing the substrate to a solution containing an anti-etch agent.

62. The method of claim 61, wherein the anti-etch agent is ammonium  
5 lactate.

63. The method of claim 61, wherein the anti-etch agent is boric acid.

64. The method of claim 48, wherein said rinsing step further comprises immersing the substrate in a rinse bath.

65. The method of claim 64, wherein said rinsing step further comprises  
10 agitating the rinse bath.

66. The method of claim 65, wherein the rinse bath is agitated with megasonic energy.

67. The method of claim 65, wherein the rinse bath is agitated by bubbling a gas through the rinse bath.

15 68. The method of claim 67, wherein CO<sub>2</sub> is bubbled through the rinse bath.

69. The method of claim 67, wherein  $N_2$  is bubbled through the rinse bath.
70. The method of claim 48, further comprising pre-rinsing the substrate with a non-aqueous solvent subsequent to said exposing step but prior to said rinsing step.
71. The method of claim 70, wherein the non-aqueous solvent is a polyhydric  
5 alcohol.
72. The method of claim 70, wherein the non-aqueous solvent is propylene glycol.
73. The method of claim 70, wherein the non-aqueous solvent is the same non-aqueous solvent used in the conditioning solution.
- 10 74. A method for removing dry etch residues from a semiconductor substrate comprising the steps of:  
treating a semiconductor substrate having dry etch residues thereon with a conditioning solution, wherein the conditioning solution comprises a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent.
- 15 75. The method of claim 74, wherein the fluorine source is HF.
76. The method of claim 74, wherein the fluorine source is  $NH_4F$ .

77. The method of claim 74, wherein the non-aqueous solvent is a polyhydric alcohol.

78. The method of claim 74, wherein the non-aqueous solvent is propylene glycol.

5 79. The method of claim 74, wherein the non-aqueous solvent is ethylene glycol.

80. The method of claim 74, wherein the non-aqueous solvent is tetrahydrofuran.

10 81. The method of claim 74, wherein the non-aqueous solvent is dimethylsulfoxide.

82. The method of claim 74, wherein the non-aqueous solvent is propylene carbonate.

83. The method of claim 74, wherein the non-aqueous solvent is isopropyl alcohol.

15 84. The method of claim 74, wherein the complementary acid is  $\text{H}_3\text{PO}_4$ .

85. The method of claim 74, wherein the complementary acid is a phosphate salt.

86. The method of claim 74, wherein the complementary acid is HCl.

87. The method of claim 74, wherein the complementary acid is a pH  
5 suppressant.

88. The method of claim 74, wherein the surface passivation agent is a carboxylic acid.

89. The method of claim 74, wherein the surface passivation agent is citric acid.

10 90. The method of claim 74, wherein the surface passivation agent is acetic acid.

91. The method of claim 74, wherein the surface passivation agent is EDTA.

92. The method of claim 74, wherein the surface passivation agent is an organic acid.

15 93. The method of claim 74, wherein the surface passivation agent is ascorbic acid.

94. The method of claim 74, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface passivation agent is citric acid.

95. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

96. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 90 – 98 : 0.005 – 0.009 : 0.09 – 0.5.

97. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

98. The method of claim 74, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is  $\text{H}_3\text{PO}_4$ , and the surface passivation agent is citric acid.

99. The method of claim 98, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

100. The method of claim 98, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.009 – 0.5.

101. The method of claim 98, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 : 6.5 : 0.25.

102. The method of claim 74, wherein the conditioning solution is a solution composed of approximately 0.01 to approximately 5.0 percent of the fluorine source, approximately 80 to approximately 90 percent non-aqueous solvent, approximately 1 percent to approximately 15 percent of the complementary acid, and approximately 0.001 to approximately 1.0 percent of the surface passivation agent.

103. The method of claim 74, wherein the conditioning solution is a solution composed of approximately 0.01 to approximately 5.0 percent of the fluorine source, approximately 80 to approximately 95 percent non-aqueous solvent, approximately 0.003 percent to approximately 1.0 percent of the complementary acid, and approximately 0.001 to approximately 1.0 percent of the surface passivation agent.

104. The method of claim 74, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

105. The method of claim 74, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

106. The method of claim 74, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

5 107. The method of claim 74, wherein said exposure step is performed for a time sufficient to substantially remove all dry etch residues from the substrate.

108. The method of claim 74, wherein said exposure step is performed for approximately 60 seconds or longer.

109. The method of claim 74, further comprising rinsing the substrate after  
10 said exposure step.

110. A method for cleaning a wafer after a dry etch process comprising the steps of:

treating a wafer having at least one of organometallic and organosilicate residues on exposed surfaces of the wafer with a conditioning solution composed of a fluorine  
15 source, a non-aqueous solvent, a complementary acid, and a surface passivation agent until the residues are removed from the wafer.

111. The method of claim 110, further comprising rinsing the substrate after said treating step.

112. The method of claim 110, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface  
5 passivation agent is citric acid.

113. The method of claim 112, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

114. The method of claim 112, where HF, propylene glycol, HCl, and citric  
10 acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 90 – 98 : 0.005 – 0.009 : 0.009 – 0.5.

115. The method of claim 112, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

15 116. The method of claim 110, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is  $\text{H}_3\text{PO}_4$ , and the surface passivation agent is citric acid.



117. The method of claim 116, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

118. The method of claim 116, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.009 – 0.5.

119. The method of claim 116, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 : 6.5 : 0.25.

120. The method of claim 110, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

121. The method of claim 110, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

122. The method of claim 110, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

123. The method of claim 110, wherein said exposure step is performed for approximately 60 seconds or longer.

124. A method for processing a substrate with patterned photoresist on the substrate surface comprising the steps of:

providing a substrate with patterned photoresist on a surface of the substrate;

performing a dry etch process on the substrate;

5 removing any remaining photoresist from the surface of the substrate; and

exposing the substrate to a conditioning solution of a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent.

125. The method of claim 124, further comprising rinsing the substrate after said exposure step.

10 126. The method of claim 124, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface passivation agent is citric acid.

127. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 :  
15 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

128. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 :  
90 – 98 : 0.005 – 0.009 : 0.009 – 0.5.

129. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

130. The method of claim 124, wherein the fluorine source is HF, the non-  
5 aqueous solvent is propylene glycol, the complementary acid is  $\text{H}_3\text{PO}_4$ , and the surface passivation agent is citric acid.

131. The method of claim 130, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

10 132. The method of claim 130, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.009 – 0.5.

133. The method of claim 130, where HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 :  
15 6.5 : 0.25.

134. The method of claim 124, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

135. The method of claim 124, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

136. The method of claim 124, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

5 137. The method of claim 124, wherein said exposure step is performed for approximately 60 seconds or longer.

138. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

10 exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol, HCl, and citric acid in the approximate ratio 0.01-5.0 : 80-95 : 0.003 - 1.0 : 0.001-1.0.

139. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

15 exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol,  $H_3PO_4$ , and citric acid in the approximate ratio 0.01-5.0 : 80-90 : 1-15 : 0.001-1.0.

140. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol, HCl, and citric acid in the ratio 0.25 – 0.3 : 90-98 : 0.005 – 0.009 : 0.009-0.5; and rinsing the wafer.

5        141. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol,  $\text{H}_3\text{PO}_4$ , and citric acid in the ratio 0.25 – 0.3 : 90-94 : 6-7 : 0.009-0.5; and

10        rinsing the wafer.

142. A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process, said solution comprising:

hydrofluoric acid;

phosphoric acid;

15        propylene glycol; and

citric acid.

143. The solution of claim 142, wherein said solution consists essentially of hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid.

144. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.01 – 5.0 : 1-15 : 80 – 90 : 0.001 – 1.0.

145. The solution of claim 144, wherein said solution comprises approximately  
5 0.01 to approximately 5.0 percent hydrofluoric acid, approximately 1 to approximately 15 percent phosphoric acid, approximately 80 to approximately 95 percent propylene glycol, and approximately 0.001 to approximately 1.0 percent citric acid.

146. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate  
10 proportion of 0.25 – 0.3 : 6 – 7 : 90 – 94 : 0.009 – 0.5.

147. The solution of claim 146, wherein said solution comprises approximately 0.25 to approximately 0.3 percent hydrofluoric acid, approximately 6 to approximately 7 percent phosphoric acid, approximately 90 to approximately 94 percent propylene glycol, and approximately 0.009 to approximately 0.5 percent citric acid.

15 148. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.27 : 6.5 : 91.5 : 0.25.

149. The solution of claim 148, wherein said solution comprises approximately 0.27 percent hydrofluoric acid, approximately 6.5 percent phosphoric acid,

approximately 91.5 percent propylene glycol, and approximately 0.25 percent citric acid.

150. A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process, said solution comprising:

- 5 hydrofluoric acid;
- hydrochloric acid;
- propylene glycol; and
- citric acid.

151. The solution of claim 150, wherein said solution consists essentially of  
10 hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid.

152. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.01 – 5.0 : 0.003 – 1.0 : 80 – 99 : 0.001 – 1.0.

153. The solution of claim 152, wherein said solution comprises approximately  
15 0.01 to approximately 5.0 percent hydrofluoric acid, approximately 0.003 to approximately 1.0 percent hydrochloric acid, approximately 80 to approximately 99 percent propylene glycol, and approximately 0.001 to approximately 1.0 percent citric acid.

154. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.25 – 0.3 : 0.005 – 0.009 : 90 – 98 : 0.009 – 0.5.

155. The solution of claim 154, wherein said solution comprises approximately  
5 0.25 to approximately 0.3 percent hydrofluoric acid, approximately 6 to approximately 7 percent hydrochloric acid, approximately 90 to approximately 98 percent propylene glycol, and approximately 0.009 to approximately 0.5 percent citric acid.

156. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid are present in said solution in the approximate  
10 proportion of 0.27 : 0.006 : 97.5 : 0.25.

157. The solution of claim 156, wherein said solution comprises approximately 0.27 percent hydrofluoric acid, approximately 0.006 percent hydrochloric acid, approximately 97.5 percent propylene glycol, and approximately 0.25 percent citric acid.

15 158. A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process consisting essentially of a fluorine source, a complementary acid, and a non-aqueous solvent.



159. The solution of claim 158, wherein the fluorine source is hydrofluoric acid, the complementary acid is phosphoric acid, and the non-aqueous solvent is propylene glycol.

160. The solution of claim 158, wherein the fluorine source is hydrofluoric  
5 acid, the complementary acid is hydrochloric acid, and the non-aqueous solvent is propylene glycol.

161. The solution of claim 158, wherein said solution further includes a surface passivation agent.

162. The solution of claim 161, wherein the fluorine source is hydrofluoric  
10 acid, the complementary acid is phosphoric acid, the non-aqueous solvent is propylene glycol, and the surface passivation agent is citric acid.

163. The solution of claim 161, wherein the fluorine source is hydrofluoric acid, the complementary acid is hydrochloric acid, the non-aqueous solvent is propylene glycol, and the surface passivation agent is citric acid.

20

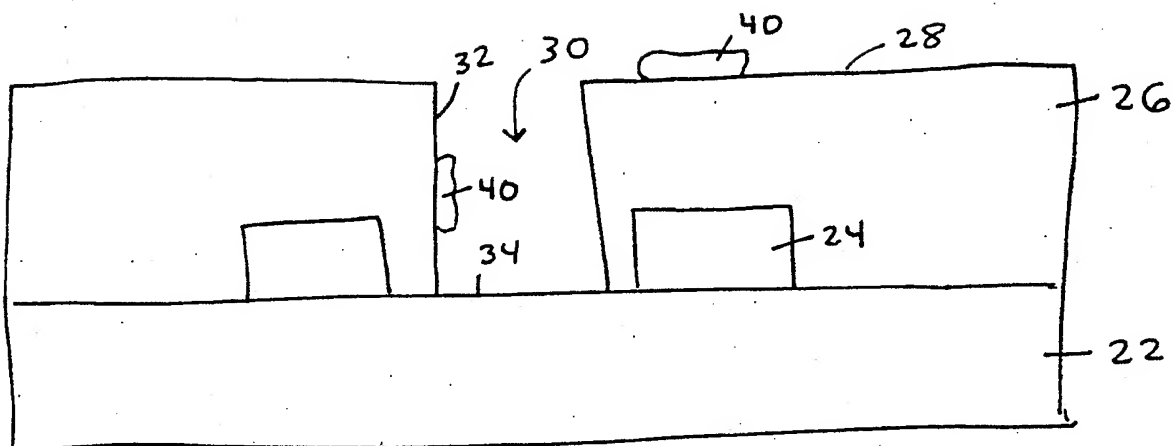


Fig. 1

20

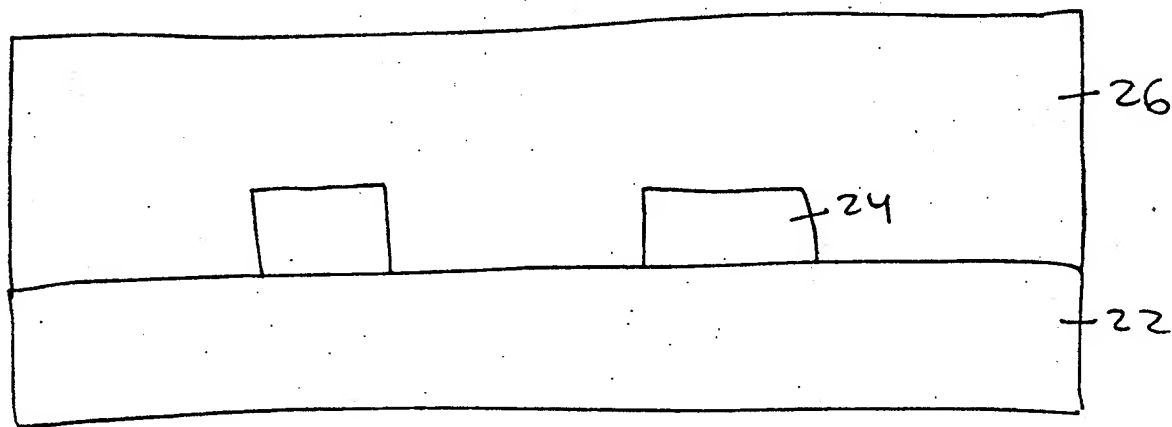


FIG. 2

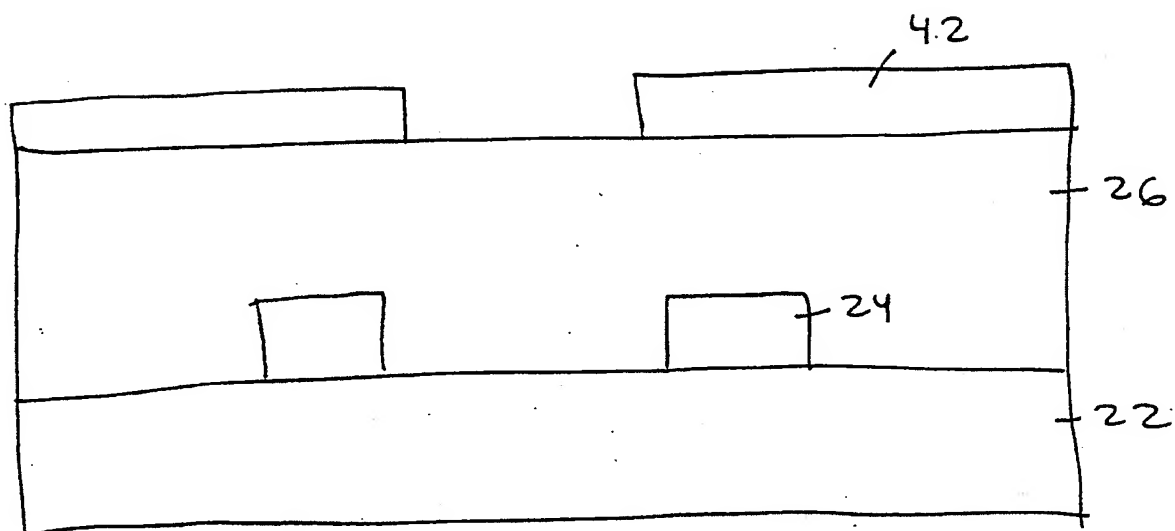


FIG. 3

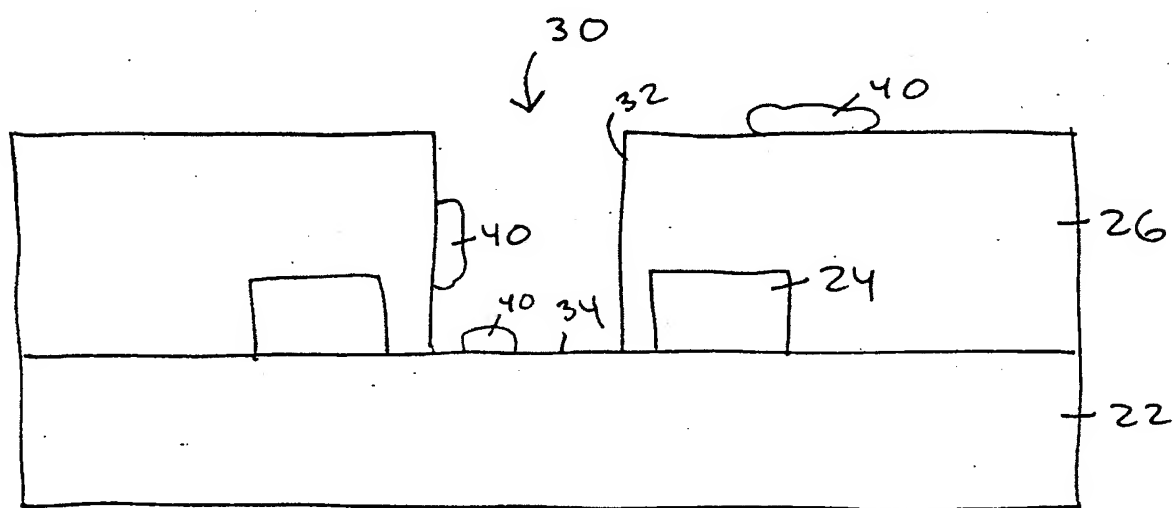


FIG. 4

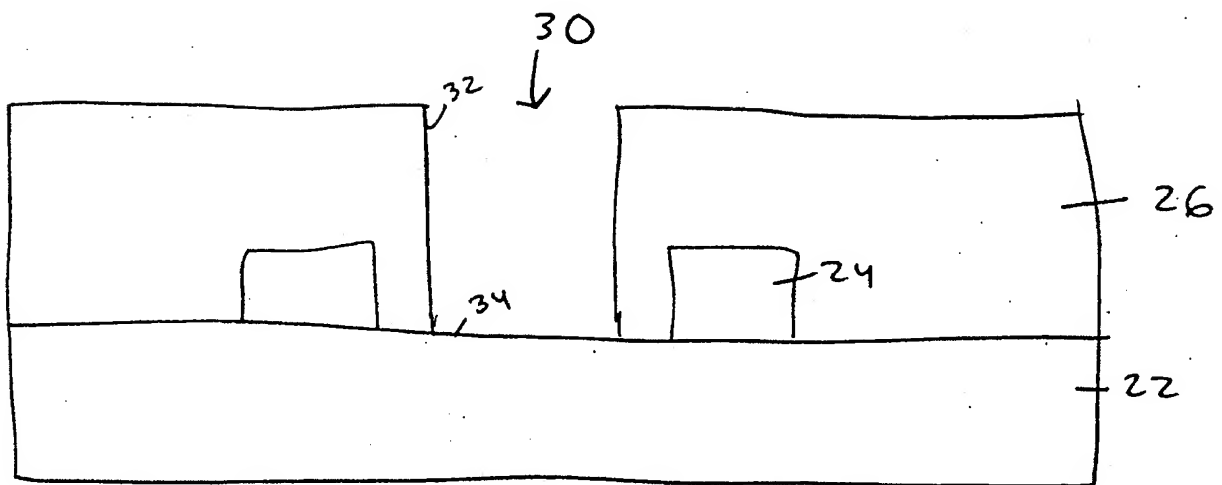


FIG. 5

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/40096

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/3213 H01L21/306 G03F7/42

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 827 188 A (MITSUBISHI GAS CHEMICAL) 4 March 1998 (1998-03-04)  the whole document	1-4, 7, 8, 10, 14, 40, 41, 43, 45-49
X	US 5 698 503 A (WARD ET AL.) 16 December 1997 (1997-12-16)  column 4, line 11-16  -/-	1, 3, 7-9, 23, 40, 41, 43, 45-48, 64-68

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

8 November 2000

Date of mailing of the international search report

17. 11. 00

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Gori, P

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/40096

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 855 811 A (GRIEGER ET AL.) 5 January 1999 (1999-01-05)	1-4, 7-10, 14-18, 23, 25, 32-35, 40-49, 59, 60, 64-73, 139, 141-149
A	the whole document ----- EP 0 812 011 A (WAKP PURE CHEMICALS) 10 December 1997 (1997-12-10) abstract -----	1

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 00/40096

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 00 40096

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 5, 6, 11-13, 19-22, 24, 26-31, 36-39, 50-58, 61-63, 74-138, 140, 150-163

Present claims 1 to 163 relate to an extremely large number of possible methods and treating solutions, and render difficult, if not impossible, to clearly determine the matter for which a protection is sought. The lack of conciseness (Art. 6 PCT) is such that a meaningful search over the whole scope of the claims is impossible.

Additionally support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found for only a very small proportion of the claimed methods and treating solutions. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Clarity is also lacking in that the nature of the complementary acid, surface passivating agent, anti-etch agent and rinsing agent used in the method is obviously dependent upon the nature of the residues and/or the semiconductor substrate. This lack of clarity also does not allow a complete meaningful search, especially in view of analysis of the inventive activity.

Consequently, the search has been restricted to a method of treating a dry etched semiconductor substrate using a solution containing

- a source of fluorine,
- H<sub>3</sub>PO<sub>4</sub>,
- a solvent of the class of polyhydric alcohols.
- possibly citric acid,

corresponding to claims 1-4, 7-10, 14-18, 23 combined with 25, 32-35, 40-49, 59, 60, 64-73, 139, 141-149.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/40096

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 827188	A	04-03-1998	JP 10055993 A	24-02-1998
			SG 60096 A	22-02-1999
			US 5972862 A	26-10-1999
US 5698503	A	16-12-1997	NONE	
US 5855811	A	05-01-1999	US 6044851 A	04-04-2000
EP 812011	A	10-12-1997	JP 10072594 A	17-03-1998